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**A Raman Spectroscopic and Electrochemical Study on Photoinduced Crystal Growth of  
DABCO Polyiodide Upon a Silver Electrode**

by

T. Ozeki and D.E. Irish

Prepared

for

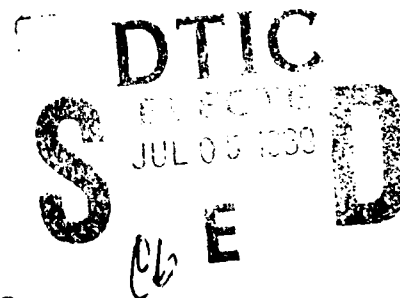
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<p>Surface Raman spectra of a silver electrode contacting with an acidic solution containing triethylenediamine (DABCO) and sodium iodide showed some new Raman peaks, which were neither the peaks of dissolved DABCO species nor of iodide. These were ascribed to diprotonated DABCO polyiodide crystal, formed and attached onto the laser-irradiated site of the silver electrode. Several facts implied that laser illumination used for the Raman measurement promoted the growth of the crystal; the possibility of photoinduced electrochemical crystal formation was suggested. The mechanisms for this local crystal growth of diprotonated DABCO polyiodide on the silver electrode was examined, as to its dependence upon the solution composition and applied potential.</p>					
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**A RAMAN SPECTROSCOPIC AND ELECTROCHEMICAL STUDY OF THE  
PHOTOINDUCED CRYSTAL GROWTH OF DABCO POLYIODIDE  
UPON A SILVER ELECTRODE**

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A large number of studies of Surface Enhanced Raman Scattering (SERS) from organic molecules adsorbed on silver electrodes have been reported. Recent studies of triethylenediamine (DABCO) carried out in our laboratory (1-3) have been extended and the results are presented below. When the Raman spectrum of an acidic solution of DABCO was measured in the presence of sodium iodide new Raman peaks were observed in addition to those due to the dissolved DABCO species and electrode-adsorbed iodide, as shown in Fig. 1-C. These new bands were ascribed to the diprotonated DABCO polyiodide crystal, formed and attached onto a laser-irradiated site of the silver electrode. Several facts suggest that the laser irradiation, applied for the Raman measurement, promoted the crystal growth; the possibility of so-called 'photoinduced electrochemical crystal growth' was suggested.

## Experimental

A Dilor OMARS-89 spectrometer with microscope, interfaced to an IBM-AT computer, was used for the measurements. The 514.5 nm line of an Argon ion laser was used as an excitation light source. The working electrode was a silver rod of 5 mm diameter sealed inside an 8 mm diameter Teflon sheath, which was assembled in an electrochemical Raman cell specially designed for use under the microscope. The surface of the silver was polished with 0.3  $\mu\text{m}$  alumina slurries on metron cloths. A platinum wire was used as counter electrode; silver wire, immersed in 1 M NaI solution, was used as reference electrode; a salt bridge separated the sample solution from the inner solution of the reference electrode.

## Results and Discussion

Raman spectra of an alkaline solution (pH 10.77, Fig. 1-A) and a slightly acidic solution (pH 6.23, Fig. 1-B), both containing 0.1 M DABCO and 0.5 M NaI, gave peaks ascribed to the bulk species of DABCO or to the electrode-adsorbed iodide ion. However, two additional peaks 220 and 160  $\text{cm}^{-1}$ , were observed in the Raman spectra of an acidic solution such as pH 0.23 (Fig. 1-C); the peak at 110  $\text{cm}^{-1}$ , which was observed for all pH values, was also strongly enhanced in the acid solution.

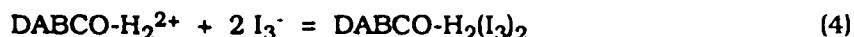
After keeping the potential of the silver electrode at +100 mV for several hours and simultaneously irradiating the surface with the 514.5 nm laser line at 300 mW, the growth of needle-like crystals was observed in the acidic solution, radiating out from the focal center of the laser beam on the electrode surface as shown in Fig. 2. This crystal did not disappear even at -100 mV, but completely disappeared at -150 mV. The cyclicvoltammogram of the acidic solution differs significantly in shape from those of the near-neutral and alkaline solutions as shown in Fig. 3. In the acidic solution, oxidation current starts to flow already at -0.08 V; and reduction current remains small up to -0.15 V. This potential was consistent with the

potential where the crystal disappeared. The Raman peaks at 200 and 160  $\text{cm}^{-1}$  observed at anodic potential also disappeared at -150 mV as shown in Fig. 4.

In order to identify these Raman peaks, several Raman measurements were carried out: (1) for the silver iodide film covering silver metal in air, (2) for the solution containing only sodium iodide, (3) for the solution containing iodide ion and iodine (the formation of  $\text{I}_3^-$  is observed), (4) for pure iodine crystal, etc. (Fig. 5). Experimental results suggest that the 220  $\text{cm}^{-1}$  peak should be ascribed to iodine ( $\text{I}_2$ ), formed by the photodecomposition of the silver iodide; the 120 and 160  $\text{cm}^{-1}$  peaks are ascribed to the symmetric and asymmetric stretching vibrations of  $\text{I}_3^-$ , formed by the reaction between  $\text{I}_2$  and  $\text{I}^-$ .

A calculation of equilibria as to the dissolved DABCO species suggests that the major species in the solutions with pH 10.77, 6.23 and 0.23 are unprotonated, monoprotated, and diprotated DABCO, respectively.

These facts suggest the following reaction mechanism for the crystal growth, observed for the acidic solution under laser light irradiation:



Thus a net reaction can be represented as follows:

(Ag)



Electrochemically-formed silver iodide (Eq. 1) is photodecomposed to atomic silver and iodine (Eq. 2). The iodine forms triiodide ion with another iodide ion which comes by diffusion from the bulk solution (Eq. 3), and is fixed upon DABCO ion (Eq. 4). These steps (Eq. 1 to 4)

are repeated (Fig. 6), and the needle-like crystal growth results at the laser-irradiated site of the silver surface. Light illumination, acidic solution, and anodic potential are required to cause the crystal growth to proceed.

In the above explanation, the participation of the triiodide ion is assumed. However, there is the possibility that more highly aggregated iodide ion such as  $I_5^-$  is participating in the reaction. So far this point remains unclear.

### **Acknowledgement**

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2. D.A. Guzonas, D.E. Irish, and G.F. Atkinson, Langmuir, 1989, 5, 787.
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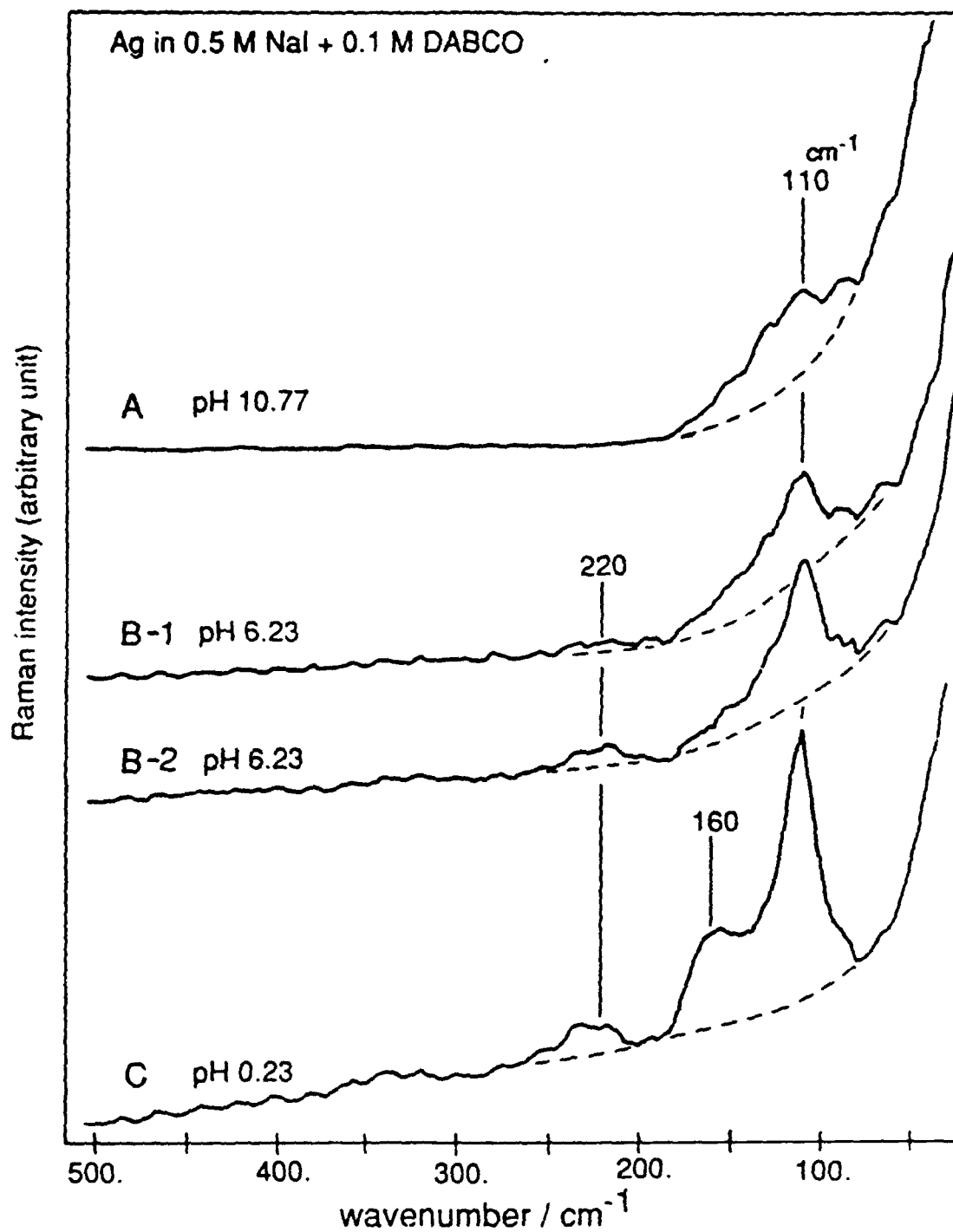


Fig.1 Surface Raman spectra of silver metal in 0.5 M NaI and 0.1M DABCO solutions with A:pH 10.77, B:pH6.23 C:pH0.23. B-2 is the spectrum after the illumination of laser light of 514.5 nm 100mW for 60min.

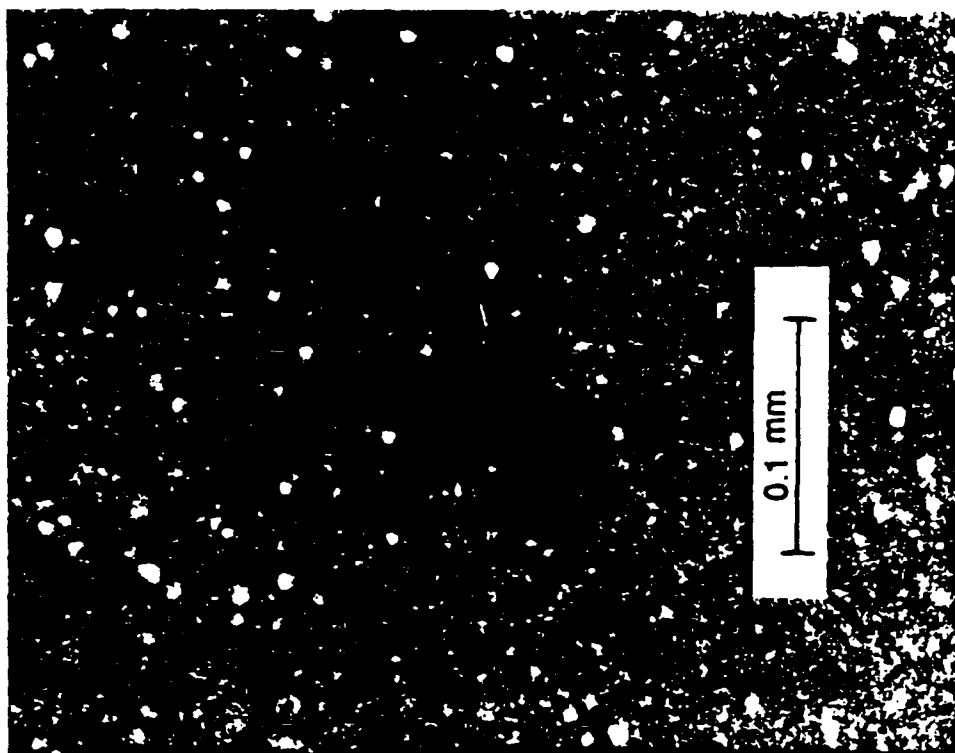
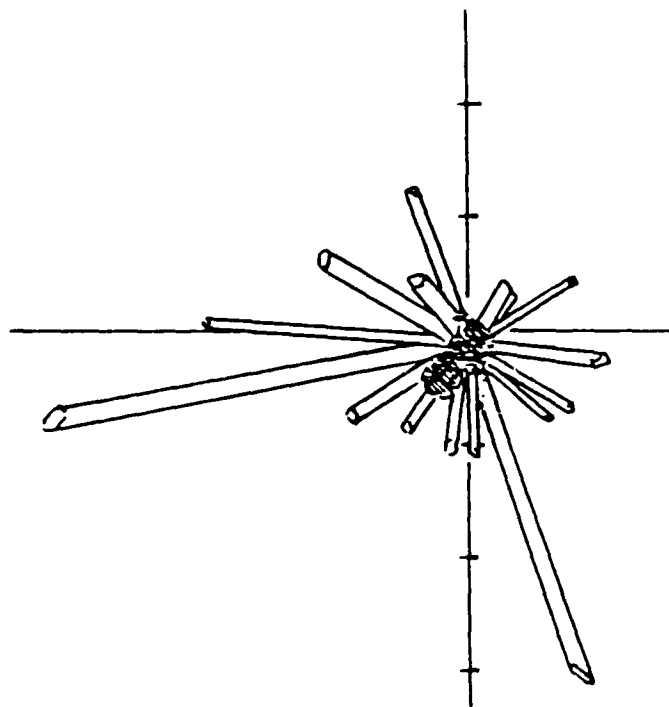


Fig.2 Typical examples of diprotonated triiodide crystal upon silver electrode found 3h after kept at +100mV under 514.5 nm 300mW laser illumination.



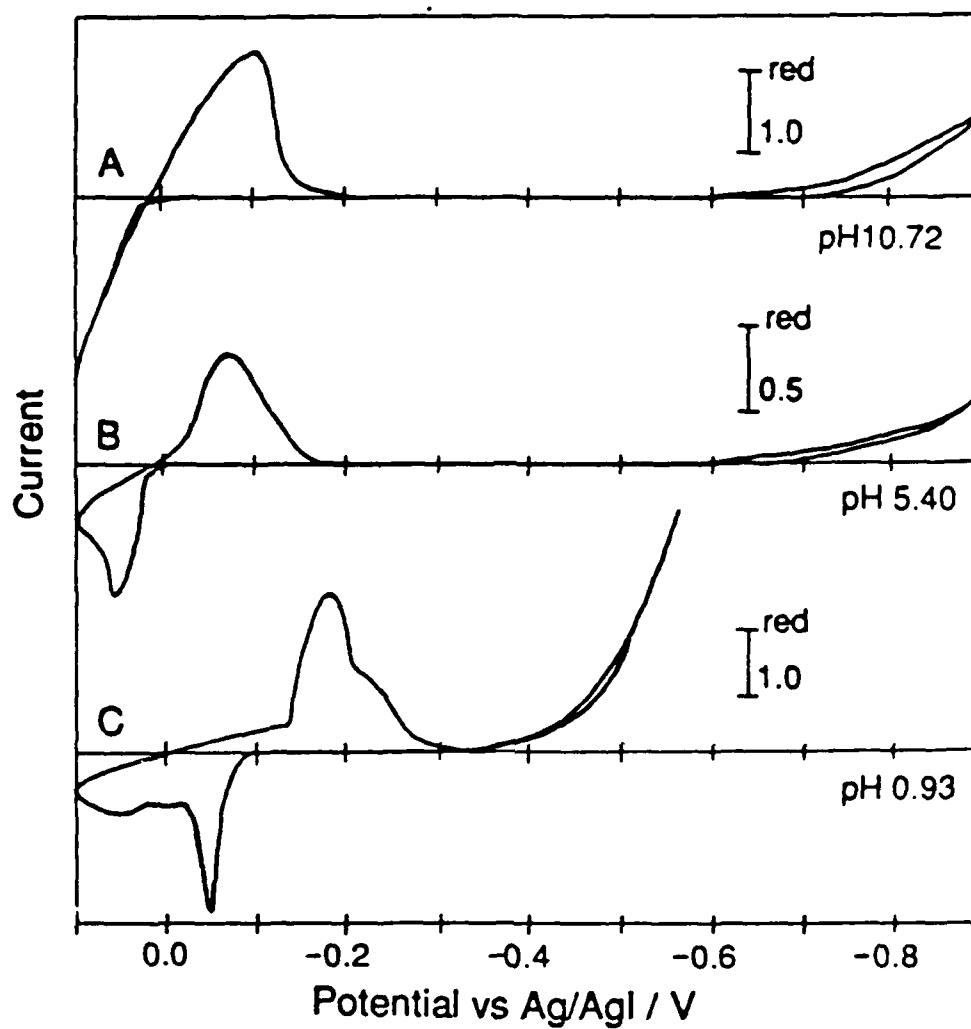


Fig.3 Cyclicvoltammograms of 0.5 M NaI and 0.1M DABCO solutions with A:pH10.72, B:pH5.40 and C: pH 0.93. Scan rate is 10 mV / s.

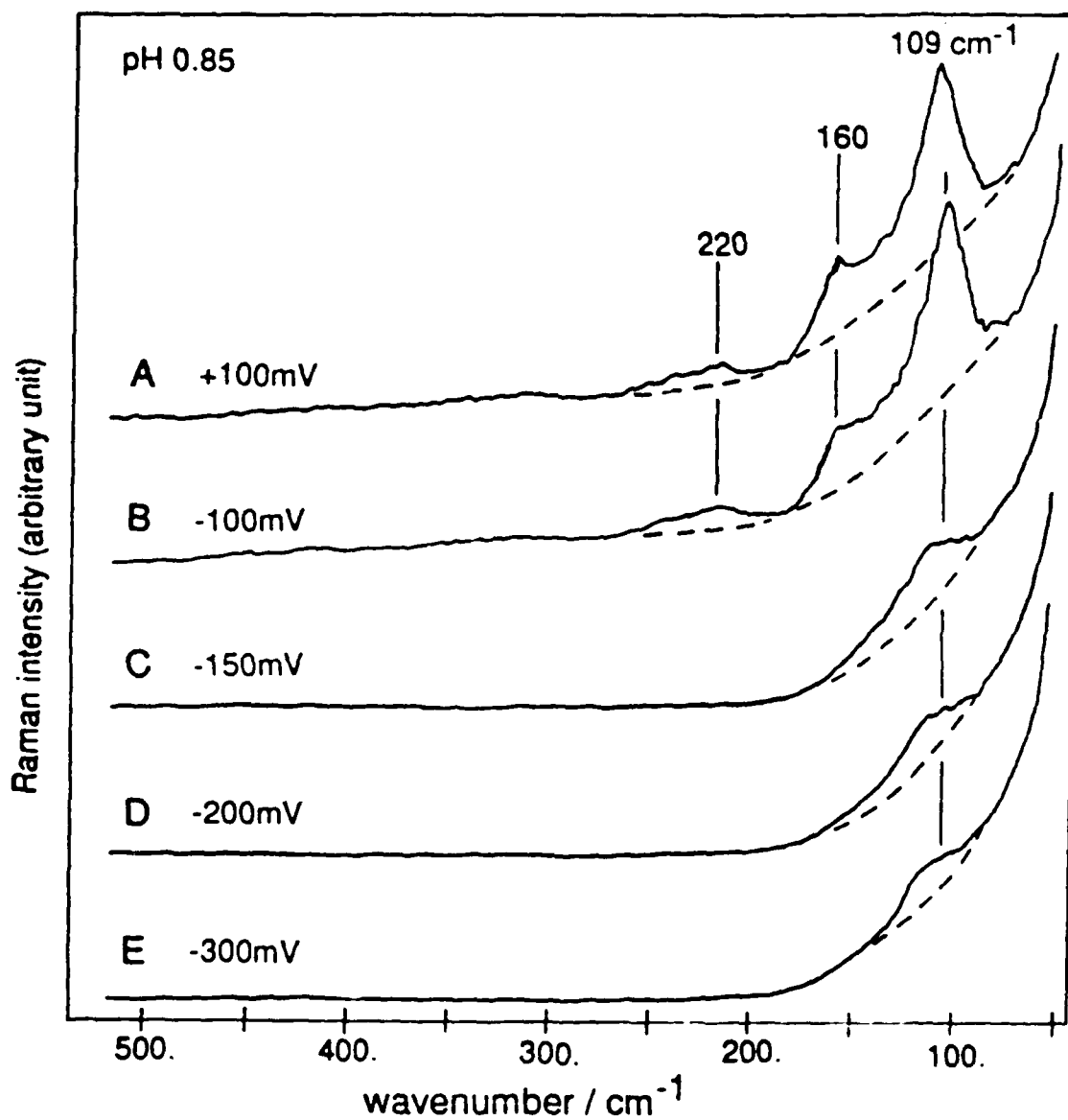


Fig.4 Dependence of surface Raman spectrum of silver electrode upon the electrode potential for 0.5 M NaI and 0.1M DABCO solution with pH0.85.

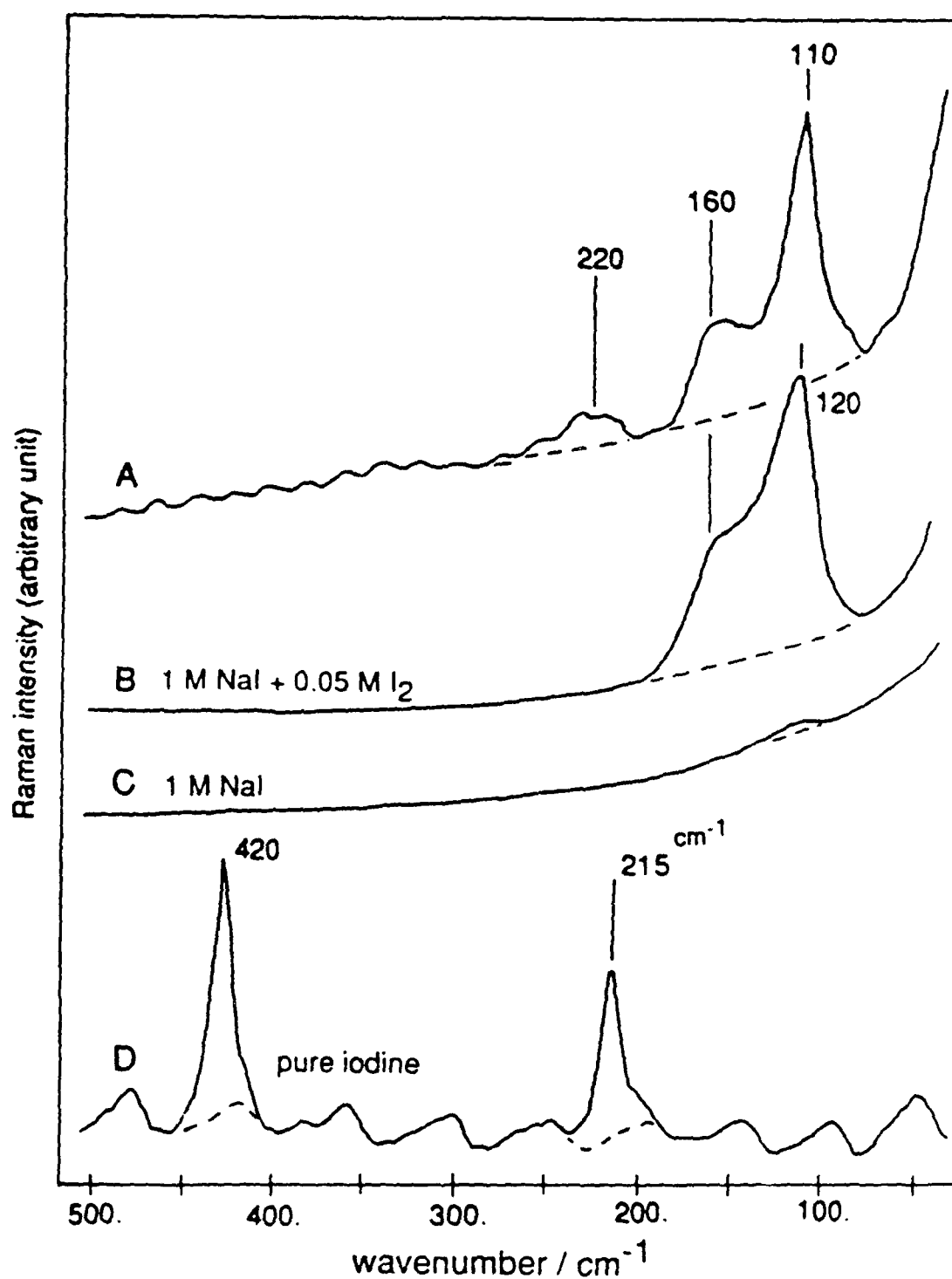
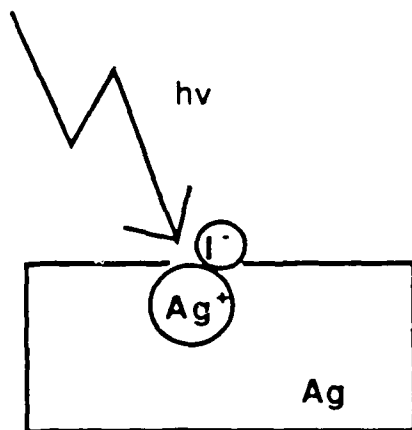


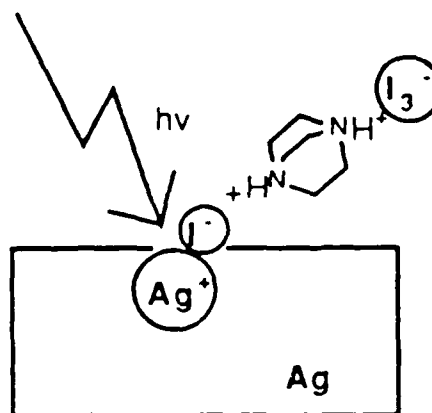
Fig.5 Comparison of several Raman spectra: A, surface Raman spectrum of silver metal in 0.5M NaI and 0.1M DABCO solution with pH 0.23; B, bulk Raman spectrum of 1M NaI + 0.05M  $\text{I}_2$  solution; C, bulk Raman spectrum of 1M NaI solution; and D, surface Raman spectrum of pure iodine crystal.

Figure 6 Schematic illustration of diprotonated DABCO triiodide crystal formation upon silver electrode.

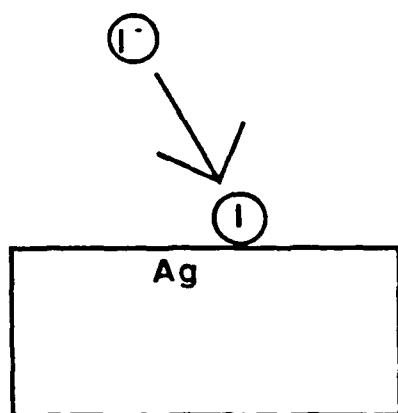
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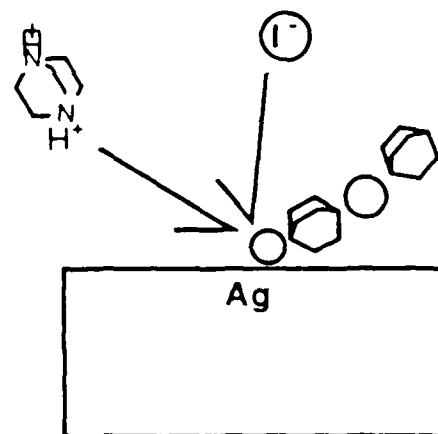
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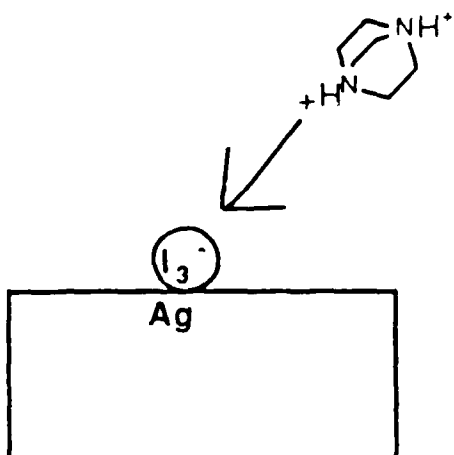
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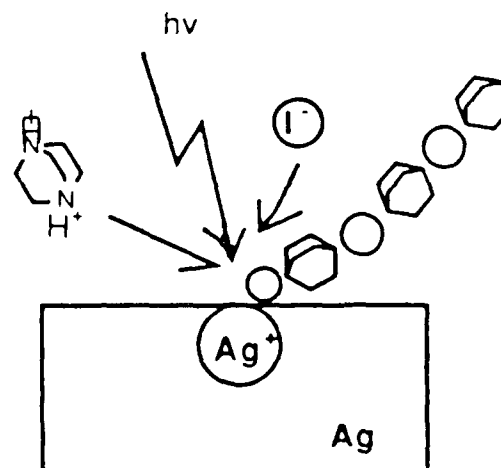
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